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APPLICATION OF A MICRO RETORT TO PROBLEMS IN SHALE PYROLYSIS

By

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INTRODUCTION

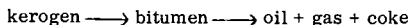
Research on the pyrolysis of oil shale (a non-shale rock that contains little or no free oil) has been popular in recent years. Despite a century of experience in the commercial production of shale oil in Scotland and elsewhere, and multifarious suggestions for effecting heat transfer, the retorting process had been little improved with respect to the considerable portion of the potential oil yield that had been lost because of excessive coke formation. The idea of using hydrogen under pressure to increase the yield and improve the quality of shale oil had been reduced to practice in the laboratory as early as 1932 (9). More recently, intensive effort has been aimed at the eventual commercialization of hydro-retorting (14).

Much of our existing knowledge of the composition of shale oil--mainly from research at the Bureau of Mines--has been reviewed by Thorne (16). The oil is highly olefinic, contains large proportions of sulfur, oxygen, and nitrogen compounds, and smells bad. It is further characterized by an inability to be totally reevaporated to the vapors from which it was originally condensed (17). Possibly the liquefaction of the vaporized pyrolysis product is accompanied by chemical condensation reactions.

Efforts to elucidate the chemistry of the pyrolysis process have not been entirely successful. Studies of the kinetics of shale pyrolysis have yielded apparent activation energies ranging from 13.6 to 48.5 kcal./mol, but mostly above 40 (5). The conclusion is usually drawn that most of the oil- and gas-forming reaction involves the breaking of carbon-carbon bonds. The reaction is rather more complicated than a simple first-order reaction. Most shales contain a small amount of organic matter that can be extracted with solvents and consists of an array of C<sub>13</sub> to C<sub>33</sub> hydrocarbons (16) along with other material. The amount of extractibles is greatly increased by heating at moderate temperatures--275 to 325°C. Credit for this discovery goes to S. R. Zimmerly (M. S. Thesis, Univ. Utah, 1923) (10). This primary decomposition process, leading to solubility, was believed to be the rupture of thermally unstable crosslinks.

Quite independently, Kogerman and Kopwille (9) in 1932 described the pyrolysis of Estonian kukersite in terms of the initial formation of a soluble, non-volatile, semisolid intermediate substance at temperatures below 360°C. At higher temperatures, according to their view, the intermediate is cracked to oil, gas, and large amounts of coke; but if the reaction is carried out under a hydrogen pressure of 250 kg/cm<sup>2</sup> (3560 psi) in the 380-410°C range, practically no coke is formed although coke does begin to be formed at higher temperatures, e. g., 440-450°C.

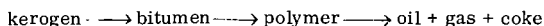
More recently, Hubbard and Robinson (6) and Allred (1,2) have accepted the idea of a "bitumen" intermediate and have expressed the mechanism as a sequence of two reaction steps.



Unfortunately, these terms are not well defined. "Kerogen" is an insoluble coal-like material with an empirical formula approximating C<sub>200</sub>H<sub>300</sub>SN<sub>5</sub>O<sub>11</sub>. The name literally means "producer of wax". The intermediate "bitumen" is a nondescript derivative of kerogen that has been thermally degraded to the point of solubility but not of volatility. "Shale oil" is the waxy liquid or solid obtained by cooling the vapors that result from pyrolysis.

Recently Hill and Dougan (5) reported on the low temperature pyrolysis of in situ shale with heated methane as the retorting fluid. Based on these studies and attendant laboratory experiments as well as published data, they suggested that at high temperatures (450-620°C) bitumen and oil are produced more rapidly than they can escape from the pores in which they are located. The diffusion-limited rates of product evolution thus account for the low apparent activation energies (13-25 kcal). During the time the initial products are confined in the pores,

polymerization occurs and subsequent decomposition of the polymer yields on the average higher molecular weight products than the primary oil. The following mechanism was proposed for high temperature pyrolysis:



However, at lower temperatures (below 427°C) the "polymer" was not necessarily an important intermediate. The activation energy for the decomposition of kerosen was said to be between 40 and 41.7 kcal; and for the decomposition of bitumen, 42.5 to 48.5 kcal.

Experimental approaches to the study of shale pyrolysis have been many and varied. Included among the few that have operated on very small samples are the thermogravimetric method (0.25–2.00 g) used by Allred (1,2) for kinetic studies, and a combination pyrolysis-gas chromatographic method (100 mg) used by Bordenave, et al, (3) to study the  $C_1$  through  $C_{11}$  portion of the product.

We have carried out an experimental program to learn more about what happens when oil-shale is heated in hydrogen or an inert atmosphere.

A versatile micro-scale (10–20 mg) retorting system has been developed. With suitable auxiliary equipment, the entire product can be examined. On the basis of kinetic experiments and some product composition data, we have concluded that diffusion-limited processes may be quite important, both in the kinetics and the chemistry of product formation.

At best, shale pyrolysis is a highly complex process that begins with the transfer of heat to a hard, non-porous rock--generally in pieces of substantial size--and ends with a residue of highly porous, friable ash. Not only is diffusion important (15) but its importance changes during the pyrolysis. The time it takes heat to diffuse into a substance that has the thermal conductivity of firebrick, and the time it takes product to diffuse out of a structure that initially has no pores is significant. Indeed, data presented by Allred (2) on the effect of particle size show that doubling the particle diameter increases by about a factor of four the time required for 95% completion of pyrolysis. The increased seriousness of the diffusion limitation at high temperatures noted by Hill and Dougan should only be compared at equal conversions. However, the extent of conversion, whether at high or low temperature, is the more important variable because porosity develops only as products leave the matrix.

It is the purpose of this paper to describe our micro-scale retort; to present some experimental results, and to suggest some possibilities and limitations for additional applications.

## EXPERIMENTAL

The oil shale for the retorting experiments was a 28 gal./ton (Fisher Assay) sample obtained from the Green River Formation in Colorado. It was crushed and screened to a particle size of 48 to 65 mesh. Detailed analyses for similar shales have been reported (7).

### Apparatus

Several systems for pyrolysis of organic compounds couples with gas chromatography have been offered commercially. None of these had sufficient control over the temperature and heating rate for kinetic studies. Preliminary experiments were done with a commercial dual column gas chromatograph with thermal conductivity detectors and designed for linear temperature programming from -65 to 400°C. As the program developed, it became evident that none of the features of this otherwise excellent instrument were particularly well-adapted for the study of shale pyrolysis. The lower limit, -65°, was not nearly cold enough for the trapping and analysis of light hydrocarbons such as methane. The upper limit of 400°C was too low for the completion of programmed temperature pyrolysis and was just at the beginning of the interesting range for isothermal pyrolysis. The linearity of temperature programming was adequate for analytical gas chromatography but was not precise enough for kinetic studies. The thermal conductivity detectors were not suitable for either kinetic or composition studies because of sensitivity to water in the products of pyrolysis. Furthermore, the oven temperature required to prevent condensation in the product transfer line (375°C) was much too high for efficient thermal conductivity detection. Dual column operation to compensate for column bleed turned out to be ineffective because no known substrate could withstand the high temperatures required for elution of the recondensation products of shale pyrolyzate. In the final version we used either no column at all (kinetic experiments) or a series of columns from which product could be eluted at safe temperatures.

The apparatus as it eventually evolved is shown schematically in Figure 1. It consisted of a pyrolysis tube mounted in a GLC oven equipped with a hydrogen flame ionization detector.

The oven served as a heater for transfer line A as well as a heated environment for pyrolysis chamber C, and also served as a programmed temperature heater for the GLC analysis of products in Traps 1, 2, and 3. Traps 2 and 3 also served as fractionating columns.

The pyrolysis unit is shown in Figure 2. It consisted of a well-insulated 30-inch length of 1/8-inch o.d. thinwall stainless steel tube with electrical connections for resistance heating. One lead was attached at the mid-point and the other to the two ends. The high current at low voltage necessary for resistance heating was supplied by a 5-volt transformer in series with a Powerstat (0-100 volt variable autotransformer). The temperature was controlled with a time proportioning device (TempTendor, API Instruments Co., Chesterland, Ohio) designed for isothermal operation. However, it was readily adapted as a linear temperature programmer by simply replacing the set knob with a sprocket and driving with a slow speed motor.

The manostat and flow controller (See Figure 1) for use with hydrogen or deuterium consisted of two ordinary hydrogen pressure regulators; the one at the inlet to the pyrolysis chamber reduced cylinder pressure to the desired operating pressure (500 psig); the downstream one, at the outlet from the last trap, reduced pressure from the operating pressure to some lower value appropriate to the pressure drop across the metering orifice. The metering orifice consisted of a 15-foot length of 0.01 inch i.d. copper tube. Hydrogen flowed at 50 ml./min. with the pressure drop set at about 35 psi. When helium was to be used as the retorting fluid at atmospheric pressure, the flow was controlled by the flow controller of the GLC unit, usually at 35 or 50 ml./min.

The trapping system consisted of three traps in series; each consisting of a length of 1/8-inch o.d. thinwall stainless steel tube coiled to fit inside a 1/2 pint Dewar. Trap 1 consisted of an 18-inch section filled with 50-mesh glass microbeads; Trap 2 contained a 30-inch section packed with 1% polyphenyl ether (nominally heptamer) on Chromosorb G; Trap 3 was a 6-foot column packed with Poropak Q (unsupported polystyrene, 50-80 mesh powder).

## Procedures

Kinetic data were obtained by taking the product through the heated transfer line directly to the detector. The choice of hydrogen flame detection limited retorting fluids to inert gases (helium) at atmospheric pressure. The operation could be either temperature programmed--usually 4°C/minute--or isothermal. In the isothermal operation at temperatures from 100 to 400°C, the temperature was raised in a progressive stepwise manner and held at each level for an extended period. Above 400°C, reaction was much faster and a fresh shale sample was used for each temperature.

Composition data were obtained by collecting the product in the traps and subsequently chromatographing each trap. The operation could be either temperature programmed or isothermal. The retorting fluid could be either hydrogen or deuterium or an inert gas (helium) under atmospheric or elevated pressure.

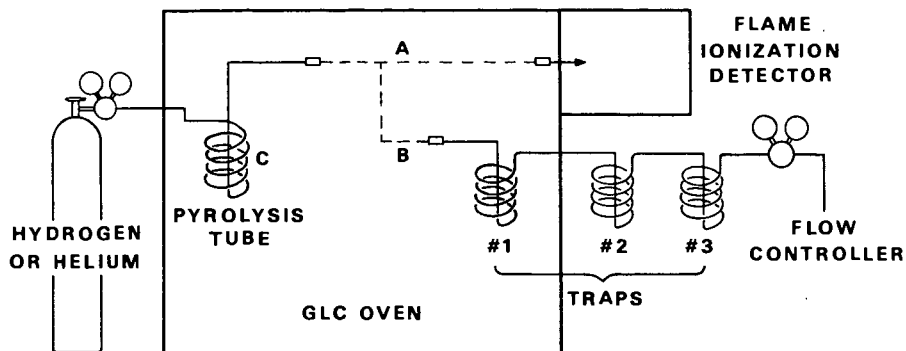
During a pyrolysis run Trap 1 was at ambient temperature while Traps 2 and 3 were cooled with liquid nitrogen. At the completion of pyrolysis the gas inlet was reconnected to the helium flow controller and, with helium flowing at 35 ml./minute, Trap 1 was heated by programming the oven to 180°C at which point the product had been eluted through C<sub>28</sub>. Further elution was prevented by immediately cooling Trap 1. At this point Trap 2 contained all products from C<sub>1</sub> through C<sub>28</sub>. Trap 2 was warmed by replacing the liquid nitrogen Dewar with one containing water at ambient temperature for two minutes. This operation transferred the C<sub>1</sub> through C<sub>6</sub> hydrocarbons to Trap 3. Since all valves had been eliminated from the product zone, each trap was mounted in the oven by means of Swagelock connectors and chromatographed in turn.

The glass bead column (Trap 1) was chromatographed merely for the purpose of obtaining a material balance. Its main function was to keep high boiling components out of Trap 2. Stripping of the glass bead column required temperatures up to 415°C. We have observed in other experiments that the stripping is accompanied by thermal decomposition, from which we conclude that some condensation or polymerization had occurred following the initial pyrolysis. It is not known whether the polymer in the glass bead trap was due to polymerization that occurred within the liquid film on the glass beads, or whether polymer was formed earlier and got into the glass bead column by entrainment in the sweep gas.

The polyphenyl ether column (Trap 2) was chromatographed from ambient temperature to about 220°C at 4°C/min. for recovery of the C<sub>6</sub> through C<sub>28</sub> components. Separation was adequate for analysis by carbon number. The maximum temperature is well below the onset of column bleed (ca. 250°C) so that columns are long-lived and dual column operation is unnecessary.

The Poropak Q column (Trap 3) contained the C<sub>1</sub> through C<sub>6</sub> hydrocarbons. With this strongly retentive substrate, only methane was eluted at subambient temperature. By simply replacing the liquid nitrogen Dewar with an empty Dewar, the methane was eluted in six or seven

**FIGURE 1**  
**APPARATUS FOR PYROLYSIS**  
**OF OIL SHALE AND ANALYSIS OF PRODUCT**



**FIGURE 2**  
**PYROLYSIS CHAMBER AND CONTROLS**

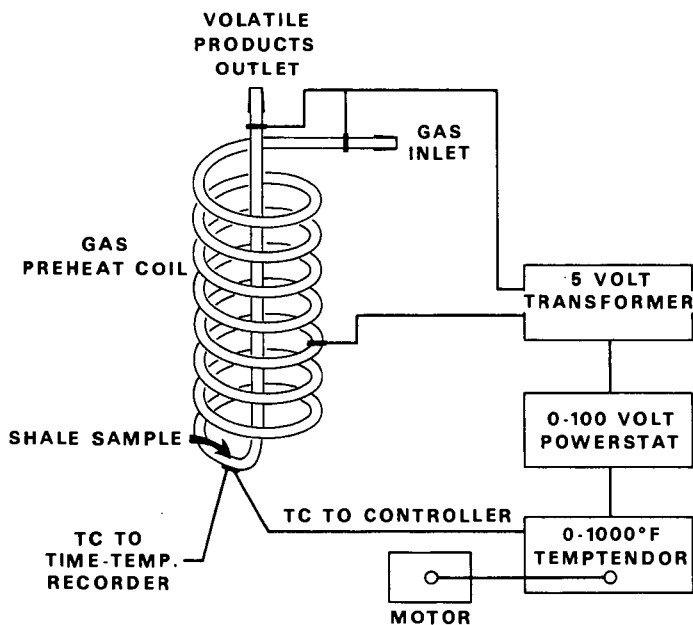
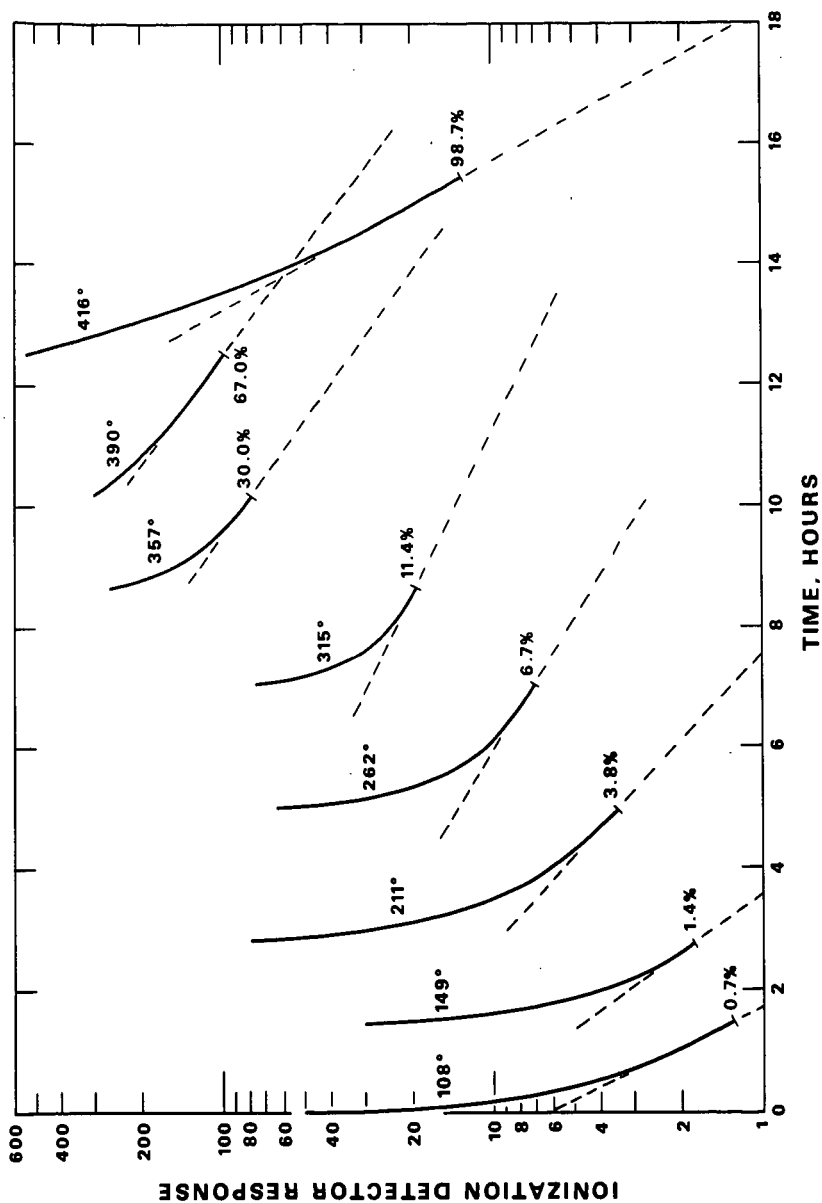


FIGURE 3

STEPWISE ISOTHERMAL PYROLYSIS OVER THE TEMPERATURE RANGE, 108 TO 416°C



minutes, after which the Dewar was removed and the GLC oven was programmed to 180°C at 4°C/min. The remaining components were eluted in the order: ethylene, ethane, propylene, and propane. Isomer separation is complete. The C<sub>4</sub>'s, C<sub>5</sub>'s, and C<sub>6</sub>'s were completely separated by carbon number but the isomers overlapped. The C<sub>4</sub> olefins were separated from the C<sub>4</sub> paraffins and from each other on a benzyl cyanide-silver nitrate column prepared by the ASTM standard procedure.

## EXPERIMENTAL RESULTS

### Isothermal Pyrolysis

Heat transfer to the small sample of small shale particles, each of which was in contact with the surface of the pyrolysis tube, was so efficient that deficiencies in the thermal control were more readily detected by changes in the rate of product formation than by variations in the observed temperature. The entire temperature range--from the lowest at which product was detected (ca. 100°C) to decomposition rates that were too fast to be measured accurately--was covered. At temperatures much below 400°C, decomposition was never quite complete even after prolonged heating. At any given temperature an initially high rate of product formation settled down to the essentially exponential decay that is characteristic of a more or less first order reaction.

A typical isothermal experiment covering the lower part of the temperature range is detailed in Figure 3. The shale sample (196 mg.) was heated at a sequence of temperatures in a helium stream, the product being swept directly to the flame ionization detector. The amplified output of the detector was replotted on a semi-log scale to show the exponential first-order decrease following the initially more rapid decline in product rate. The heating was continued at the lined-out condition to establish the slope for later extrapolation to "ultimate yield" at that temperature. At the conclusion of each period the temperature was quickly increased and the process repeated at successively higher temperatures until the decomposition was complete. The temperature and percentage yield of product actually obtained in each interval are recorded on the graph. The results of extrapolation to infinite time in two such experiments are plotted in Figure 4. The term "ultimate yield" comprises only the organic compounds to which the flame ionization detector responds. Such products as hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, and water are excluded. The ultimate yield increased exponentially with temperature until the point of complete decomposition of the kerogen was reached at about 400°C. The ultimate yield approximately doubles in each 42°C temperature interval.

Isothermal pyrolysis rates in the range above 400°C were very fast. Estimates of the time required to reach 50%, 90% and 99% conversion are given in Table I. By way of comparison, the programmed temperature (4°C/min.) pyrolysis reached 50% conversion at about 428°C, at which point the rate constant was about 13%/min.

Table I

### ISOTHERMAL PYROLYSIS RATES AT HIGH TEMPERATURE

Temp., °C	<u>Minutes to Indicated Conversion</u>		
	<u>50%</u>	<u>90%</u>	<u>99%</u>
430	2.5	14	60
440	1.5	7	30
450	0.8	5	21
460	0.5	3.7	16
470	0.3	3	14
480	-	2.6	12
490	-	2.3	11
500	-	2.1	10
510	-	1.9	9.3
520	-	1.7	8.7
530	-	1.6	8

At high conversions, i. e., near the end of the reaction, the rate of product formation was slow enough for the kinetics to be followed. Plots of the product yield as a function of time for about the last 13% of the product at selected temperatures between 417 and 485°C are shown in Figure 5.

FIGURE 4  
ULTIMATE PRODUCT YIELD AS A  
FUNCTION OF PYROLYSIS TEMPERATURE

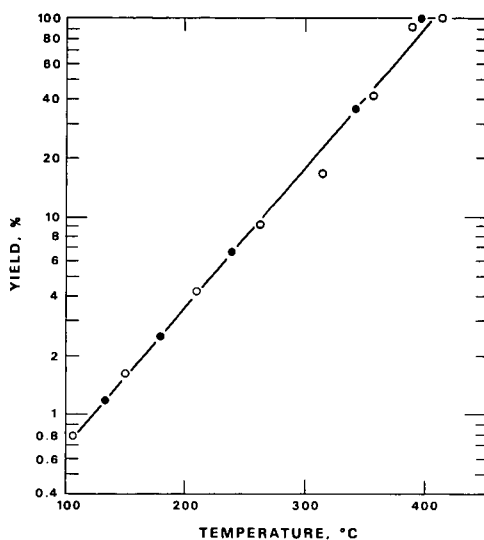


FIGURE 5  
RATE OF FORMATION OF THE LAST 13% OF PRODUCT

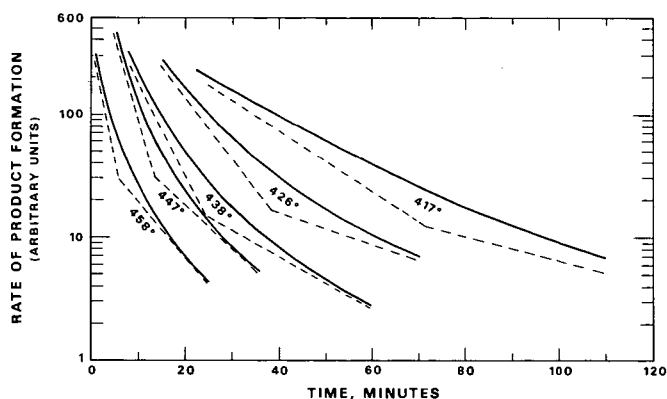
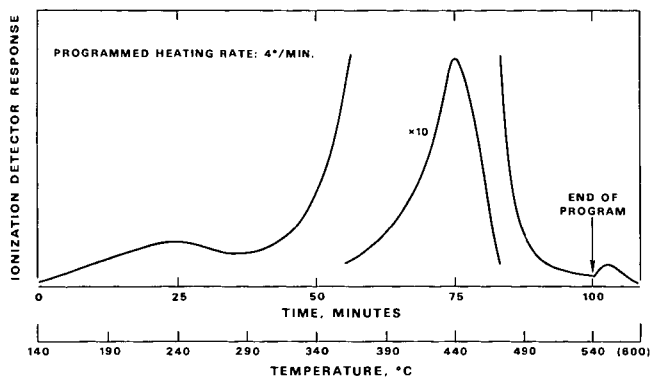


FIGURE 6  
GLC TRACE FOR OIL SHALE PYROLYSIS



### Programmed Temperature Pyrolysis

A GLC trace for a programmed temperature experiment is reproduced in Figure 6. The products of pyrolysis of a 21.4 mg sample of shale were swept to the flame ionization detector while the temperature was increased from 80 to 540°C at the rate of 4°C/minute. In contrast with the isothermal experiments, the rate of kerogen decomposition is steadily increasing. The rate of product formation also increases and passes through a maximum at about 440°C. Product formation is nearly complete at 540°C and after a short period at 600°C, no more is detected. A remarkably similar plot was obtained by Allred (2) by a thermogravimetric method.

By integrating the area under the curve from left to right, one obtains the cumulative yields as a function of temperature that are shown in Table II. By integrating in the opposite direction, i.e., from right to left, one obtains ratios of the instantaneous rate of product formation at any temperature to the amount of product yet to be formed. These "rate constants" for the "decomposition of kerogen" are also listed in Table II.

Table II

### RATE CONSTANTS AND CUMULATIVE PRODUCT YIELD AS A FUNCTION OF TEMPERATURE

<u>Pyrolysis</u> <u>Temp., °C.</u>	<u>K, Wt. %/min.</u>	<u>Cumulative</u> <u>Yield, Wt. %</u>
170°	0.067	0.34
186	0.090	0.64
204	0.113	1.02
220	0.122	1.49
236	0.145	2.01
252	0.131	2.56
268	0.099	3.01
284	0.106	3.40
300	0.132	3.83
316	0.192	4.42
332	0.340	5.38
349	0.615	6.91
366-	1.096	9.9
383	2.07	15.1
400	3.80	23.2
417	7.19	37.5
425	11.62	47.0
434	18.77	60.6
442	25.80	75.0
451	33.27	87.0
468	24.47	97.4
485	12.75	98.9
502	9.10	99.3
519	9.36	99.5
536	8.62	99.7
(600)		(100.0)

Methane comprises about 3% of the total product. A "methane only" experiment was carried out by pyrolyzing 52 mg of shale and simply trapping all heavier products in an 18-inch section of 1/8-inch o. d. copper tube, coiled to fit into a 1/2-pint Dewar and inserted between Trap 1 and the flame ionization detector (See Figure 1). Whereas methane is held indefinitely on organic substrates at liquid nitrogen temperature, the empty tube condensed and held C<sub>2</sub> and higher products but did not retain any methane. The transmit time for methane through the traps was under 60 seconds and tailing was not a problem. The GLC trace for methane was generally similar to that for total product, except that little or no methane was produced below about 275°C. The 3% of total product that appeared below 275°C must therefore have been produced by a mechanism different from the one that produced methane. Both curves peak at about 440°C. A distinction should be made between the rate of product formation (detector response) and the rate constant for kerogen decomposition (rate of product formation relative to amount of product yet to be formed, i. e., amount of kerogen remaining). The rate constants reach their maxima at about 450°C, at which point the cumulative yield of methane was only 31% compared with 87% for total product. The cumulative yield of methane as a function of temperature and the rate



FIGURE 7  
PROGRAMMED TEMPERATURE PYROLYSIS OF SHALE

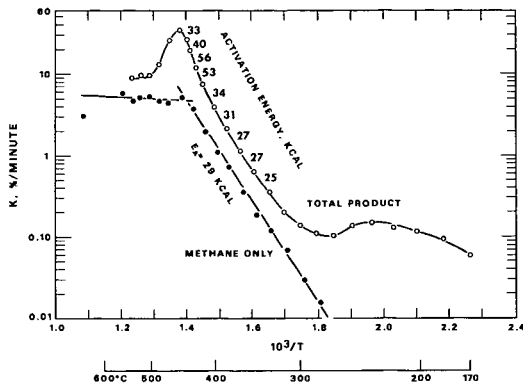


FIGURE 8  
ISOTHERMAL PYROLYSIS OF  
ACTIVATION ENERGY OF SHALE

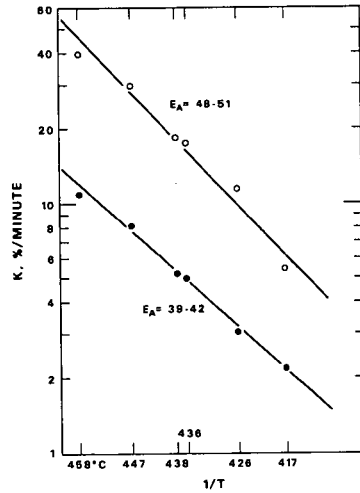
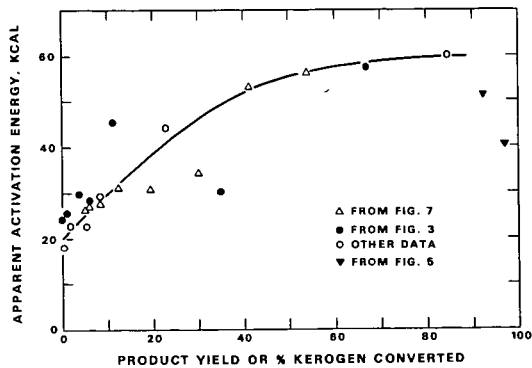


FIGURE 9  
ACTIVATION ENERGY FROM MICRORETORTING



constants as a function of methane-yet-to-be-produced are in Table III.

Table III

RATE CONSTANTS AND CUMULATIVE METHANE YIELD  
AS A FUNCTION OF TEMPERATURE

<u>Pyrolysis</u> <u>Temp., °C</u>	<u>K, %/min.</u>	<u>Cumulative</u> <u>Yield, %</u>
280	0.015	0.03
295	0.028	0.10
312	0.065	0.26
330	0.112	0.52
346	0.180	1.04
362	0.335	1.90
380	0.700	3.4
395	1.05	4.8
412	1.90	11.0
430	3.60	18.8
448	4.98	31.4
466	4.43	44.6
484	4.53	53.7
503	5.06	62.6
519	4.94	69.6
535	4.49	75.2
555	5.5	79.7
(650)		(100)

To evaluate the effect of mineral constituents on the pyrolysis reaction, limited work was done on kerogen that had been concentrated by extracting the shale with hydrochloric acid to remove carbonates, hydrofluoric acid and remove silicates, ammonia to remove mineral acids, and  $\text{CHCl}_3$  and benzene to remove natural bitumen. Pyrolysis gave a GLC trace very similar to that for raw shale, including a few percent of low temperature pyrolyzate. However, this product contained much larger proportions of normally gaseous hydrocarbons. The possible mechanistic significance, i. e., the effect of infinite porosity, was not appreciated at that time and unfortunately a "methane only" experiment was not done.

Product Composition

High retorting temperatures are known to give increased proportions of light paraffins and aromatic compounds (4). The kinetic experiments described in the foregoing section confirmed the earlier report of Bordenave, et al, (3) that the composition of the product also changes with the extent of pyrolysis. Thus, in a programmed temperature experiment, nearly 70% of the methane was in the last 13% of the product.

Many experiments were carried out in which the product was trapped and examined by gas chromatography. In one set the shale was heated isothermally in a helium stream for 30 minutes at each of a series of temperatures, much as in Figure 3, and the products were collected separately for each temperature. In the first few fractions, representing the first few percent of product, a rather narrow distribution of carbon numbers that shifted to higher values with increasing temperature suggested cuts from a simple distillation. Thus, a product collected at 126°C was mainly  $\text{C}_{11}$  to  $\text{C}_{15}$ ; at 200°C at least 90% was in the  $\text{C}_{14}$  to  $\text{C}_{22}$  range; at 220°C it was largely  $\text{C}_{20}$  to  $\text{C}_{24}$ ; at 275°C it was mostly  $\text{C}_{22}$  to  $\text{C}_{26}$ , but traces of methane and other light products were beginning to appear. At 303°C the main product was  $\text{C}_{25}$  to  $\text{C}_{31}$  but the cut-off at  $\text{C}_{31}$  was sharp and the amount of light products had increased. At 325°C and higher, a dramatic change occurred. The  $\text{C}_{31}^+$  fraction was large and considerable amounts of methane and other products gave a continuous spectrum of GLC peaks.

A large peak between  $\text{C}_{17}$  and  $\text{C}_{18}$  and perhaps other smaller but outstanding peaks may be members of the isoprenoid series. Odd-numbered normal hydrocarbons are also a little more abundant than the even-numbered members. In isothermal pyrolysis at a given high temperature the initial product is lower in methane and richer in higher molecular weight components than the later portions.

### Pyrolysis Under Hydrogen or Deuterium Pressure

The pyrolysis conditions selected for present purposes were: temperature programmed at 4°C/minute, 500 psig hydrogen (or deuterium) pressure with a sweep rate of 50 ml/minute (measured at atmospheric pressure).

Typical product distributions obtained under 500 psig hydrogen are compared in Table IV with that obtained with helium at atmospheric pressure. Also included are data reported by Schlinger and Jesse (14) for a large pilot plant operation in which the hydrogen pressure was in the range of 1000 to 2000 psig--flow rate not specified--and the shale was crushed so that the largest chunks did not exceed 4 inches in diameter.

Table IV

#### PRODUCT DISTRIBUTION FROM RETORTING IN HYDROGEN AND HELIUM

Component, Wt. %	Sweep Gas		
	Helium	Hydrogen	
		Present Work (a)	Schlinger & Jesse
Methane	3.0	22.8	6.2
Ethylene	1.9	3.8	
Ethane	1.6	8.0	3.3
Propylene	1.6	4.7	
Propane	1.1	12.0	2.4
C <sub>4</sub>	2.7	6.9	0.8
C <sub>5</sub>	2.9	3.3	0.1
C <sub>6</sub>	3.0	3.5	22.7 <sup>(b)</sup>
C <sub>7</sub> - 12	15.8	12.2	
C <sub>13</sub> - 28	40.9	21.6	64.5 <sup>(b)</sup>
C <sub>29</sub> <sup>+</sup>	25.4	1.2	

(a) The actual yield in hydrogen was 193% of that in helium.

(b) Estimated to a weight basis from the reported ASTM Distillation.

The effect of hydrogen in our experiments was to increase the over-all yield to about 190% of that with helium. The increase was reflected in every category except the C<sub>29</sub><sup>+</sup> fraction. The yield of methane was increased enormously. So were those of ethane and propane, but not at the expense of ethylene and propylene. The absolute yields of ethylene and propylene were actually about 3.8 and 5.7 times larger, respectively, in the presence of hydrogen than in the presence of helium.

The substitution of deuterium for hydrogen offered an intriguing possibility for the study of mechanism. Unfortunately, our deuterotorting experiments yielded only fragmentary data. Isotopic analyses of methane, ethylene, ethane, propylene, and propane are possible by high-resolution mass spectrometry, although the C<sub>3</sub> hydrocarbons require the highest resolution of which the instrument is capable. Fortunately, in the spectra of the butenes, the difference in ionizing voltage between the C<sub>4</sub>H<sub>8</sub><sup>+</sup> (parent) and C<sub>4</sub>H<sub>7</sub><sup>+</sup> ions is sufficient to permit isotopic analysis by conventional low-resolution mass spectrometry.

The few available bits of data are shown in Table V. In a low-deuterium-pressure experiment (160 psig, 50 ml/minute flow) all possible isotopic species of methane and ethane were present. The major species of methane were CH<sub>3</sub>D (methane-d<sub>1</sub>) and CD<sub>4</sub> (methane-d<sub>4</sub>). The most abundant ethane was C<sub>2</sub>H<sub>5</sub>D (ethane-d<sub>1</sub>). In another experiment at 500 psig deuterium pressure, an isotopic distribution was obtained on cis-butene-2. All possible isotopic species were present. Whatever mechanisms may be operative, the end result was to substitute some or all of the hydrogens with deuterium without saturating the double bond. The k's in the tabulation amount to a statistical analysis. The random k's are computed from the coefficients of the binomial expansion of (h+d)<sup>8</sup>; the observed k's are computed from the experimental results

such that

$$k_1 = \frac{d_1^2}{d_0 \times d_2}, \text{ etc.}$$

Comparison of the random and observed k's shows a small but significant preference for even numbers of deuteriums in the olefins.

Table V

ISOTOPIC SPECIES IN METHANE, ETHANE AND  
CIS-BUTENE-2 FROM DEUTEROTORTING SHALE.

Isotopic Species	Methane %	Ethane (a) %	<u>cis-Butene-2</u>		
			%	k <sub>obs</sub>	k <sub>random</sub>
d <sub>0</sub>	19	12	30.6		
d <sub>1</sub>	23	24	18.9	0.75	2.29
d <sub>2</sub>	16	20	15.6	1.24	1.75
d <sub>3</sub>	16	16	10.4	0.86	1.60
d <sub>4</sub>	26	12	8.1	1.17	1.56
d <sub>5</sub>		8	5.8	0.83	1.60
d <sub>6</sub>		8	5.0	1.72	1.75
d <sub>7</sub>			2.5	0.40	2.29
d <sub>8</sub>			3.1		

(a) Not better than  $\pm 4$ .

## DISCUSSION

The changes of product rate with temperature from which activation energies are calculated were measured in a variety of kinetic experiments. The results can be correlated over three broad ranges of conversion: 0-40%, 40-87%, and 87-100%.

### Activation Energies

Isothermal pyrolysis experiments, such as the example in Figure 3, in which the temperature was increased stepwise yielded apparent activation energies from incipient pyrolysis to about 85% conversion. Because the time intervals were short and the temperature increases moderate, one should not expect large changes in the structure of the kerogen or in the nature of the product being formed during the short intervals of abrupt temperature increase.

The programmed-temperature experiment (Figure 6) yielded a set of rate constants that gave the Arrhenius plot shown in Figure 7. Activation energies were calculated from the slopes at selected temperatures in the range of 316 to 440°C (4.4-75% conversion). The anomalous decline in the rate constants for the last 13% of product in the programmed temperature pyrolysis (Figure 7) is explained by the fact that these rate constants are expressed on a weight-yield rather than a molar basis. The increase in lower molecular weight products, and especially methane, must reflect changes in the structure of the uncracked residue as it approaches coke. The change in slope suggests negative activation energies. However, reasonable values for this region can be obtained from the isothermal pyrolysis data in Figure 5 by treating the product rate curves as a linear combination of a fast and slow reaction, i.e., fast and slow on a weight yield basis. The "slow" reaction becomes rate-controlling at about 96-97% conversion. The Arrhenius plot in Figure 8 for the rate constants of these reactions gives apparent activation energies of about 40 for the slow reaction and 50 for the fast reaction.

Apparent activation energies from the isothermal and programmed-temperature experiments are plotted in Figure 9 as a function of the extent of pyrolysis. The initially low values rise as pyrolysis proceeds, and reach the 50-60 kcal/mol range after 40% conversion. This corresponds quite closely to the point at which Allred (1) inferred from the data of Hubbard and Robinson (6) that the decomposition of kerogen to bitumen was complete. From here forward, the reaction appears to follow first-order kinetics and the observed activation energies are in excellent agreement with the 57.1 kcal reported by Keith, et al, (8) for the thermal cracking of a petroleum gas oil. The agreement is good enough to suggest that the last 60% or so of the pyrolysis may be relatively uncomplicated rupture of carbon-carbon bonds. However, when high temperatures are used in the later stages of reaction, the rate of product formation increases faster than the rate of diffusion, even though porosity is high; hence the drop in apparent activation energy.

#### Evidence for Diffusion Effects

In a diffusion-limited system the apparent activation energy should rise as the effects of diffusion are reduced. Thus, the good heat transfer characteristics of the micropyrolysis reactor, the small shale particle size, the small sample size, and the high sweep rate all tend to minimize the delay of getting product out. The activation energy in a large part of the reaction approaches 60 kcal and is the highest so far reported. The thermogravimetric method used by Allred (1,2) utilized a finely powdered shale and a larger sample size, but depended largely on diffusion to get the product out of the sample bucket. His highest reported activation energy in the temperature range of 430-475°C was 40.5. Only a slight effect of sample size over the range of 0.25-2.00 grams was noted.

The presence of "natural bitumen" in small amounts in raw shale, the conversion of kerogen to more bitumen by the low temperature thermolysis of weak bonds, and--as will be proposed later--the occurrence of diffusion-controlled recombination reactions are all factors that affect the kinetics in the early stages of pyrolysis.

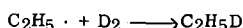
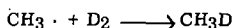
The elimination of high molecular weight products from the rock matrix during pyrolysis at low temperatures is diffusion-limited because of low porosity. The stepwise isothermal pyrolysis of 48-65 mesh shale at temperatures below 325°C gave a series of distillation-like fractions. They covered a molecular size range that was remarkably like the C<sub>13</sub> to C<sub>33</sub> range reported by Thorne (16) for solvent-extracted natural bitumen. That diffusion was a limiting factor is shown not only by the progression of molecular sizes with increasing temperature, but also by the observation that a C<sub>28</sub> fraction could be stripped from a glass bead packed column at 180°C but required a temperature 100°C higher to be stripped from small shale particles. The same lack of porosity that interferes with volatilization into the gas stream could also interfere with the extraction of natural bitumen with solvents. We have observed that extraction of the shale before pyrolysis actually made little difference in the amount (ca 3%) of low temperature pyrolyzate. Even more strangely, concentrated kerogen that had been freed of most of the minerals by extraction with acid (HCl and HF) and then further extracted with boiling chloroform and boiling benzene still yielded the low temperature material. Extraction at high temperatures under pressure has long been known to give larger bitumen extracts, but this may be a combination of low-temperature thermolysis and solvent extraction.

A very significant effect of diffusion is apparent in the differences in product yield and composition resulting from the use of hydrogen as retorting fluid. Shale particle size seems to have a considerable effect on the efficiency with which hydrogen interacts with the pyrolysis products.

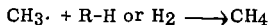
#### Free Radical Reactions

The thermal cracking process is considered to involve free radicals. In an inert sweep gas the free radicals may disappear by routes different from those in hydrogen. Data pertinent to the effect of hydrogen on product yield and composition are in Table IV. Some fragmentary results on the incorporation of deuterium in some of the smaller molecules are in Table V.

The high yields of methane, ethane, and other light products under hydrogen pressure, and the high content of the mono-deutero species (methane-d<sub>1</sub>, ethane-d<sub>1</sub>) argue for the importance of methyl, ethyl, and other small free radicals in the over-all reaction. There is no telling how many free radicals disappeared by coupling, but evidently a good many reacted with deuterium:



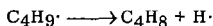
Quite a few appeared as undeuterated species, probably by abstracting hydrogen from a nearby organic molecule or from molecular hydrogen formed in the pyrolysis reaction.



Incidentally, the increased yield of light products at high pyrolysis temperatures may be a result of the increased availability of hydrogen due to the dehydrogenation of aliphatic precursors of aromatic compounds.

The large methane-d<sub>4</sub> content may well reflect the deuterogenation of coke in the latter stages of pyrolysis. The last 70% of the methane was produced along with the last 13% of the total product when the pyrolysis was done in helium. At that stage the shale is highly porous and would offer relatively little resistance to the diffusion of deuterium into the particles.

The major isotopic species in the cis-butene-2 is the undeuterated molecule. One could postulate that the most important reaction of the butyl radical is loss of an atom of hydrogen, possibly due to abstraction by another radical, or disproportionation.



The tendency toward even numbers of deuteriums in cis-butene-2 suggests that olefin bi-radicals, or even diolefins such as butadiene, might be involved in a sequence of hydrogenation-dehydrogenation reactions while slowly diffusing from the developing pores.

The product distributions in Table IV can now be compared. The product distribution obtained by Schlenger and Jesse (14) by hydrotorting large chunks of shale is not grossly different from the product distribution we obtained by retorting small shale particles with a high helium sweep rate. Unfortunately, data on the pyrolysis of large particles in an inert gas were not included. Nevertheless, Schlenger and Jesse reported a considerable absorption of hydrogen, and their product is probably quite paraffinic. The product distribution in our hydrotorting experiment is profoundly different. The yield of gaseous hydrocarbons is much increased and the C<sub>29</sub><sup>+</sup> component is almost non-existent. Evidently the improved diffusion in the micropyrolysis reactor had about the same moderating effect, in the presence of helium, on the recombination reactions as the 1000-2000 psi hydrogen pressure had in the large reactor with large pieces of shale.

Comparison of the C<sub>5</sub><sup>+</sup> product in the three cases shows:

	<u>C<sub>5</sub><sup>+</sup>, Wt. %</u>
Helium Retort	88.3
Micro-hydrotort	41.8 (x 193% = 80.6)
Large-scale Hydrotort	87.3

In terms of the recovery of liquid fuels from shale, the reduction in loss to coke was more than compensated by increased yields of normally gaseous hydrocarbons. The actual yield of liquid products was slightly reduced. Perhaps the optimum process will provide for a controlled amount of radical recombination.

#### ADDITIONAL APPLICATIONS OF THE MICRO TECHNIQUE

Because of the ease and speed of microretorting, many possibilities exist for coupling it with all sorts of specialized detection systems. Thus, one could pursue elusive details of reaction mechanism or examine the effects of process variables on product components or product distribution. As examples of the kinds of phenomena that might be examined are the following observations: a) a tendency of sulfur compounds to be formed relatively early and nitrogen compounds relatively late in the pyrolysis, and b) a tendency for the product from hydrotorting to have higher ratios of nitrogen compounds to sulfur compounds than are observed in the product from inert gas retorting.

Especially useful should be the selective sulfur (11, 12) and nitrogen (13) detectors recently developed. In the programmed temperature mode of operation, one could continuously monitor the rates of production of sulfur or nitrogen compounds. With selective traps one might monitor particular compound types, such as basic or non-basic nitrogen, or individual compounds like H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>O or CO<sub>2</sub>. In isothermal operation the same sort of thing could be done to determine whether reaction orders for sulfur- or nitrogen-containing products were the same as for hydrocarbons. In any of the variants where products are trapped and component analysis is done

subsequently, the individual sulfur and nitrogen compounds can in many cases be identified as well as measured.

Combinations of a suitable GLC column with selective traps could be further coupled with mass spectrometry for a great variety of studies, particularly with deuterium as the retorting fluid--we have only scratched the surface. One can only wonder about the isotopic compositions of the other butane and butene isomers. Would straight-chain components be more or less deuterated than branched-chain or cyclic compounds? What would be the isotopic composition of water, ammonia, or hydrogen sulfide? What would be the effect of process variables such as temperature, heating rate, particle size, and deuterium pressure on deuterium incorporation?

#### CONCLUSIONS

Pyrolysis of oil shale on a micro scale is a technique with much potential and some accomplishment.

The pyrolysis reaction appears to be a somewhat diffusion-limited first order reaction whose kinetics are complicated by the possibility of more than one bond-breaking step in going from kerogen to oil, gas, and coke.

The extent of diffusion-control diminishes during the course of the reaction as the shale changes from impervious rock to highly porous ash, and increases at high heating rates because products are generated faster than they can diffuse out of the pores.

The effect of hydrogen in hydrotorting is to compete with condensation reactions. The result is increased yields of lighter products and less coke formation.

The use of deuterium gave results that are consistent with a free radical mechanism. The thermal free radicals may become stabilized by the gain or loss of a D or H atom or, depending on the extent of diffusion control, may recondense to form heavier product.

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